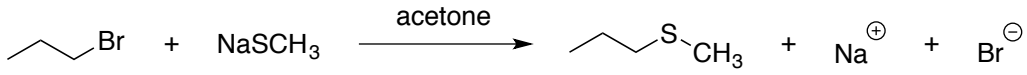
ANSWER KEY

Chemistry 233

Chapter 11 Problem Set – Pt. 1 (Substitution Reactions)

1. Consider the S_N2 reaction shown below and answer the following questions.



A. Write the rate law for the reaction.

Rate = k [~Br] [$NaSCH_3$]

B. Identify the nucleophile and the electrophile in the reaction.

Nu: $\ddot{S}CH_3$ E: ~Br electrophilic carbon

C. State how each of the following factors would affect the rate of the reaction.

a. Increasing the concentration of 1-bromopropane.

↑ Rate

b. Decreasing the concentration of $NaSCH_3$ by one-half.

↓ rate by 1/2

c. Changing 1-bromopropane to 2-bromopropane.

↓ rate 1° faster than 2°

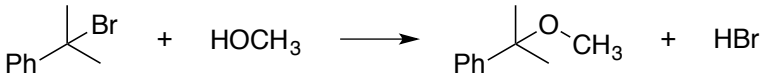
d. Changing 1-bromopropane to 1-iodopropane.

↑ rate $I^\ominus$ better LG than $Br^\ominus$

e. Changing $NaSCH_3$ to CH_3OH.

↓ rate $\ddot{S}CH_3$ is a better Nu

2. Consider the S_N1 reaction shown below and answer the following questions.



A. Write the rate law for the reaction.

Rate = k [Ph–Br]

B. Identify the nucleophile, the electrophile, and the reaction solvent.

Nu: $H\ddot{O}CH_3$ E: Ph–Br or Ph⊕

C. State how each of the following factors would affect the rate of the reaction.

a. Increasing the concentration of the alkyl halide.

↑ rate

b. Increasing the concentration of $HOCH_3$.

No change (Nu is not involved in rate law)

c. Replacing $HOCH_3$ with $NaOCH_3$.

No change

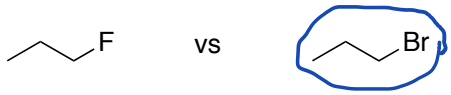
d. Changing the alkyl halide from a bromide to an iodide.

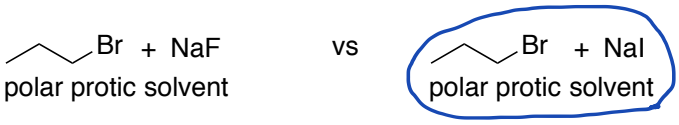
↑ rate

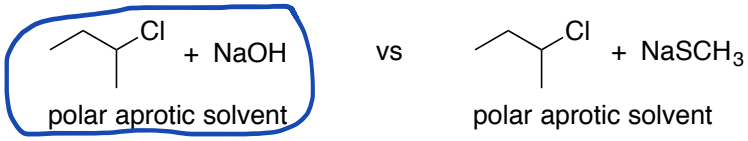
e. Changing the alkyl halide to 1-bromopropane.

↓ rate (No rxn would occur)

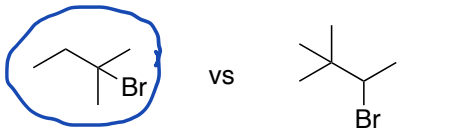
3. For each of the following pairs, circle the one that will proceed faster by an S_N2 reaction mechanism.

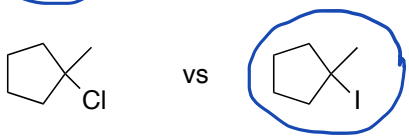


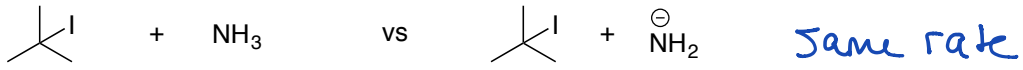


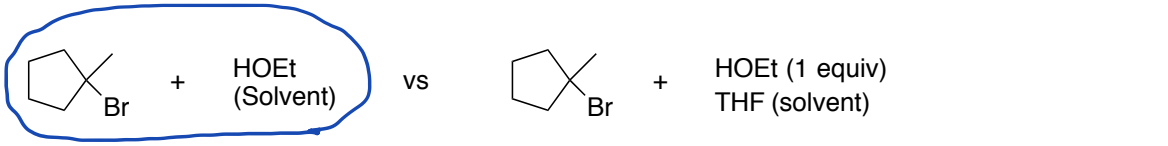


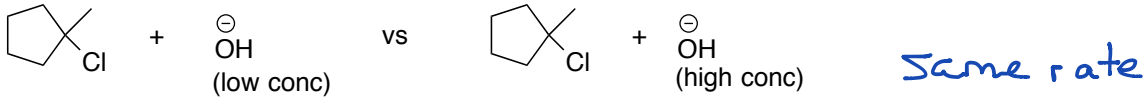
4. For each of the following pairs, circle the one that will proceed faster by an S_N1 reaction mechanism.



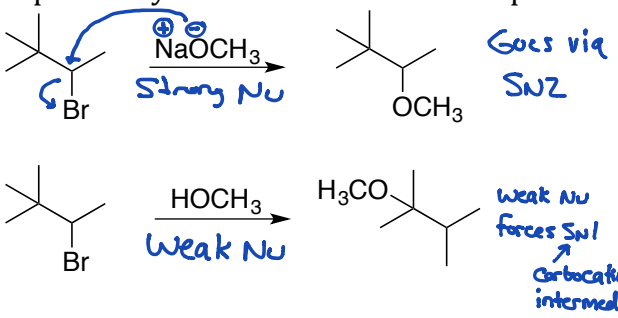




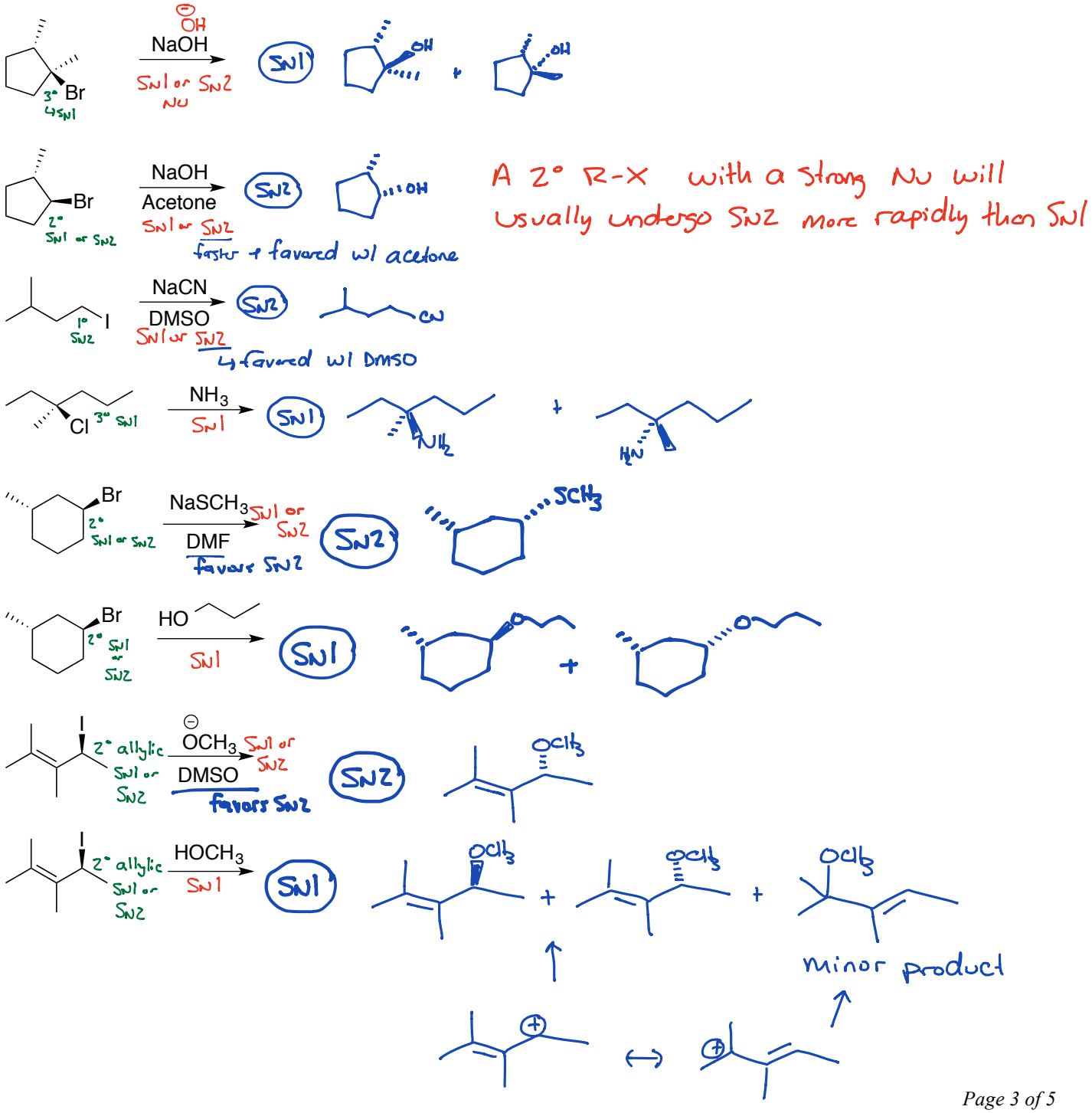


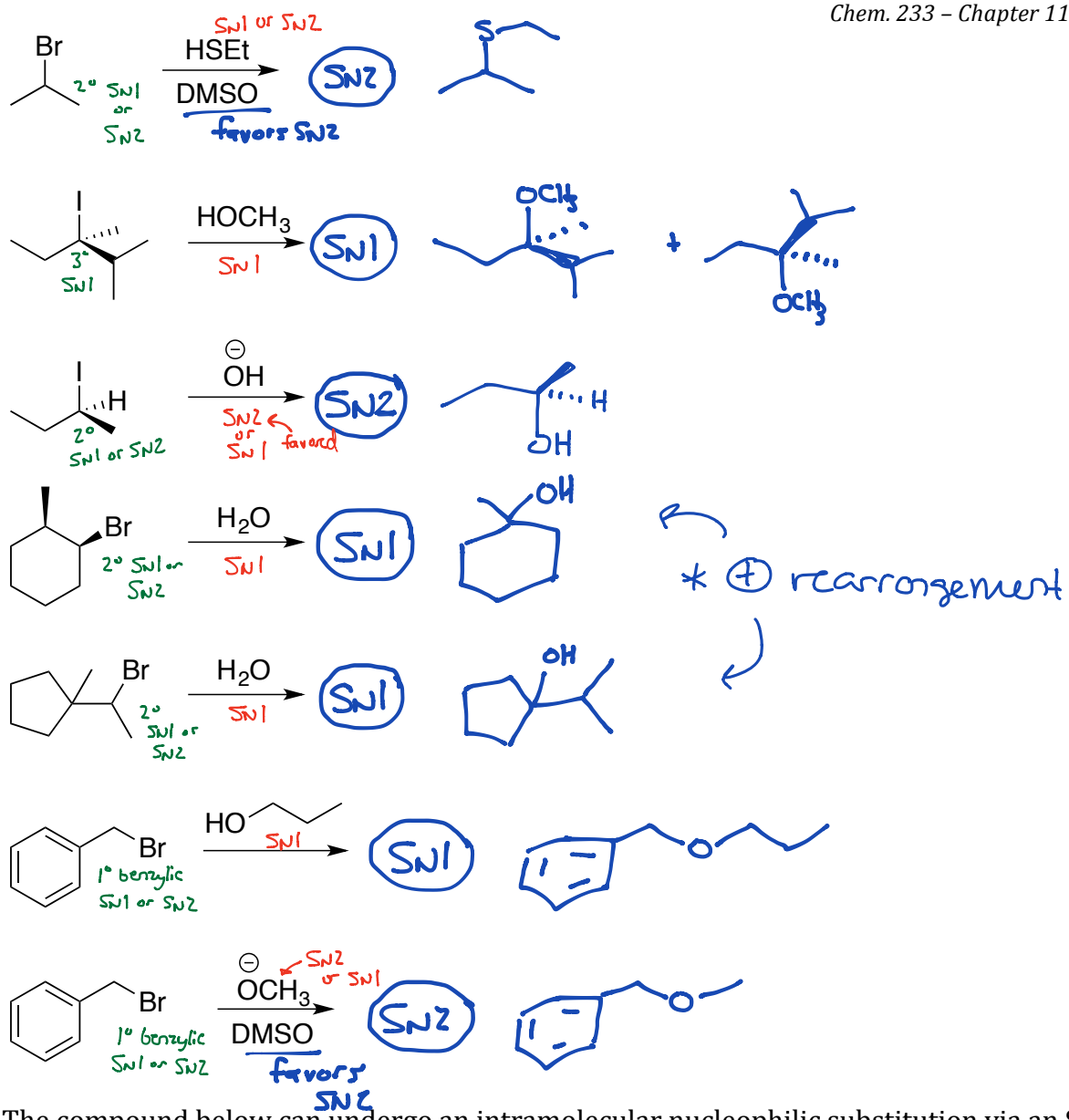


5. Explain why the two reactions below provide constitutionally different products.

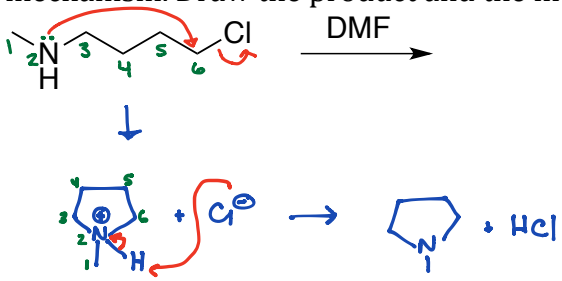


6. Assuming each reaction below undergoes nucleophilic substation, predict the mechanism (S_N1 or S_N2) and draw the major product. Include stereochemistry where appropriate.

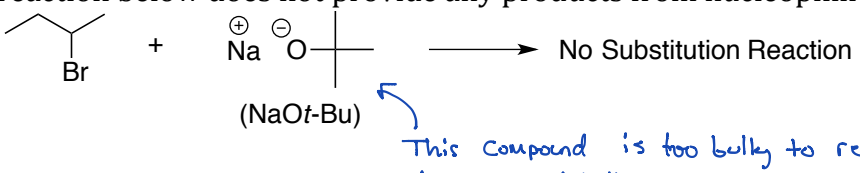




7. The compound below can undergo an intramolecular nucleophilic substitution via an S_N2 mechanism. Draw the product and the mechanism by which it is formed.



8. Explain why the reaction below does not provide any products from nucleophilic substation.

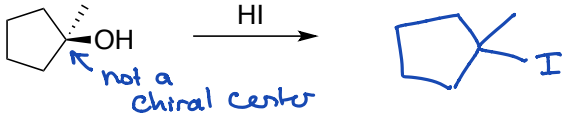


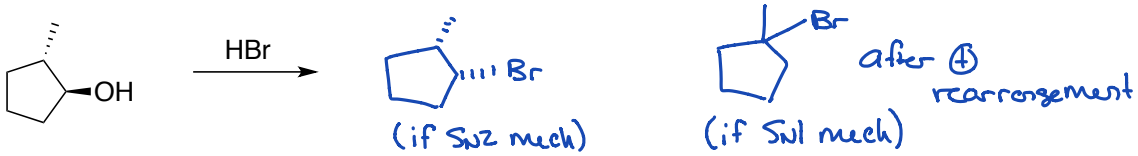
This compound is too bulky to react as a nucleophile in a substitution rxn.
(Steric hinderance between the Nu and E)
Actually leads to elimination product.

9. Predict the product(s), with correct stereochemistry for each of the following substitution reactions involving an alcohol starting material.

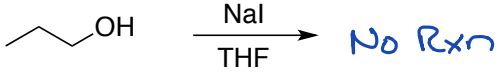
(a) 

(b) 

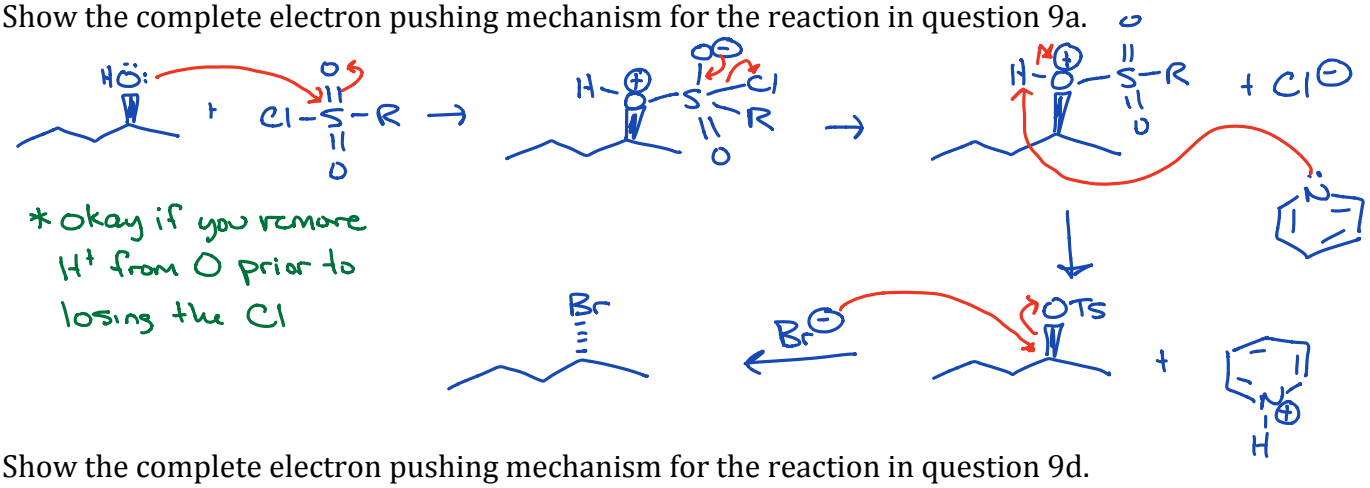
(c) 

(d) 

(e) 

(f) 

10. Show the complete electron pushing mechanism for the reaction in question 9a.



11. Show the complete electron pushing mechanism for the reaction in question 9d.